Study the Effects of Carbon Nanotube and Expandable Graphite On The Performance Of Intumescent Fire Retardant Coating

by

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Dissertation submitted in partial fulfilment of
the requirements for the
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(Mechanical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

____

(AP Dr. Faiz Ahmad)

UNIVERSITI TEKNOLOGI PETRONAS
Tronoh, Perak
July 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken by unspecified sources or persons.

YASMIN BINTI MOHD. AZMI

ABSTRACT

The aim of this project is to develop and study the effect of carbon nanotubes(CNT) on char strength and expansion of intumescent coating and compare the results with the coatings without CNTs. Intumescent formulations without and with CNT were developed and the formulations without CNTs were used as bench mark in this project.

A total of 13 formulations were developed without CNTs and tested for expansion and char strength. Based the results, a set of 4 formulations were selected for reinforcing CNTs. A total of 15 formulations reinforced with CNTs were developed. The formulation is developed by varying the percentage of CNT. Fire test and SEM were done to analyze the char strength and microstructure of char. The char expansion achieved was approximately 9 times and microstructure showed good bonding of CNT within the char.

ACKNOWLEDGEMENT

First and foremost, I would like to praise Allah the Almighty for with His blessings and guidance I am able to successfully complete my final year project. My appreciation goes to my Supervisor, AP Dr Faiz Ahmad for the advice, plans, and also for the knowledge and experiences shared during my attachment under him. His guidance had developed my interest in solar energy which helped me to develop during my final year in UTP.

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NOMENCLATURE

$NH_4H_{2H}PO_4$	Ammonium polyphosphate
NH_3	Gas Ammonia
H_3PO_4	Phosphate Acid
$2C_3H_6N_6$	Melamine
MWCNT	Multiwall Carbon Nanotube
EG	Expandable Graphite

CHAPTER 1

INTRODUCTION

1.1. BACKGROUND OF STUDY

In recent decades, the disastrous accident caused by damage of steel structure in fire has reminded people of the risk of fire in some industrial buildings and equipment. Some efficient protective ways such as application of flame retardant coatings can be used to protect steel structure in fire [1]. Under the action of heat, intumescent fire retardant coating will expand and form a thick porous charred layer to insulate the substance. The substance will be protected against high temperature rise and exposure to oxygen within a period of time. Applying this type of coating is one of the most efficient ways of providing fire retandancy to flammable materials [2].

1.2 PROBLEM STATEMENT

i. During fire breakout, the temperature of fire may increase to 1000°C.
ii. However Structure steel loses load carrying ability above 500°C which lead to major lose in term of life and money [2].
iii. The traditional coating before having a poor thermal properties—the coating oxidizes at high temperature

1.3 OBJECTIVE, SCOPE OF STUDY, AND LIMITATION

1.2.1. Objective

i. To develop the intumescent coating with and without CNTs
ii. To study the effect of carbon Nanotube (act as filler) and expandable graphite on the performance of intumescent coating

1.2.2. Scope of study

i. Research on the formulation of intumescent coating from various sources such as journals, articles, books, internet, previous report and etc.

ii. Developed the intumescent coating sample based on the 2 types of formulation with 1 particle size

   a. expandable graphite is mixed with carbon nanotube

   b. expandable graphite only

iii. Analysis of the result by doing comparison of different type carbon source sample

1.2.3. Limitation of project

- Focusing on one type of CNT only - MWCNT
- Develop formulation using one size of expandable graphite only

1.4 THE RELEVANCY OF STUDY

The main objective is to find the suitable formulation of intumescent coating using different types of carbon source and different particle size that can protect the steel substrate (carbon steel). Statistic of fire from Malaysia fire department shown that 21537 reported fire accident occurred on 2008. The number can be divided to several types of firebreak out where 3556 reported fire occurred at building (house, office, factor and etc) while 1206 reported fire started from tool and machine. As the number of fire breakout increase every year while involve money and life lose, the author felt that this is important to study the new way to protect the structural steel when a fire breakout.

CHAPTER 2
LITERATURE REVIEW

2.1 INTUMESCENT COATING

An intumescent is a substance which swells too many times their original thicknesses when exposed to fire as a result of heat exposure, thus increasing in volume, and decreasing in density [4] and it is a form of thin and thick film. Intumescents are typically used in **passive fire protection**. The applications of intumescent coating are wide-ranging and the demands for this material have significantly increased in recent years, especially in the civil engineering area to protect building structure from fire attack. The application of intumescent had extended to protection of structure steel of platform recently. An improvement of intumescent system may help the petroleum industrial company to prevent platform collapse due to fire exposure which leads to losing life and billion of money.

The coatings are designed to perform under severe conditions and to maintain the steel integrity between 1 until 3 hours when the temperature of the surrounding is in excess of 1100˚C [M. Jimenez, S. Duquesne, S. Bourbigot, 2006]. Steel is a very strong and versatile building material, but at temperatures of 500ºC it begins to lose its structural integrity, which may lead to building collapse. The role of fire protective coatings is to lengthen the time taken for the steel to reach its critical failure temperature and therefore allow occupant's sufficient time to escape and enhancing the safety of the rescue services [7]. Generally, 3 active ingredients are used bound together by binder. In this project, filler added in the ingredient to increase the char strength.

The ingredients are as followed:

i. Acid source: Ammonium Polyphosphate (APP)
APP is a high molecular weight chain phosphate and it is scarcely soluble in water. This chemical is also a source of phosphoric acid which will speeds up the formation of carbonaceous char and NH_3 which improves the swelling. Therefore, this chemical will be act as the acid source and also as the blowing agent.

ii. Carbon source (expandable graphite)
The carbon source will form a carbon char when the dehydration of the mineral acid occurs. Expandable graphite, and or carbon nanotube will used as the carbon source. Melamine and APP can also act as the carbon source of the intumescent process.

iii. Blowing agent :Melamine
Blowing agent decomposes to yield gaseous product during the intumescent process which will increase the char stability. Melamine is the most preferred blowing agent to be use.

iv. Binder (epoxy resin and hardener)
Epoxy resin will be use as the binder. Epoxy resin is a mixture of Diglycidylether of Bisphenol A (DGEBA) and polyamide. When the epoxy resin, APP derivatives and boric acid are combined together, they will produce a very hard char and this will relate to a better adhesion to the substrate.

v. Filler : Multiwall carbon Nanotube (MWCNT)

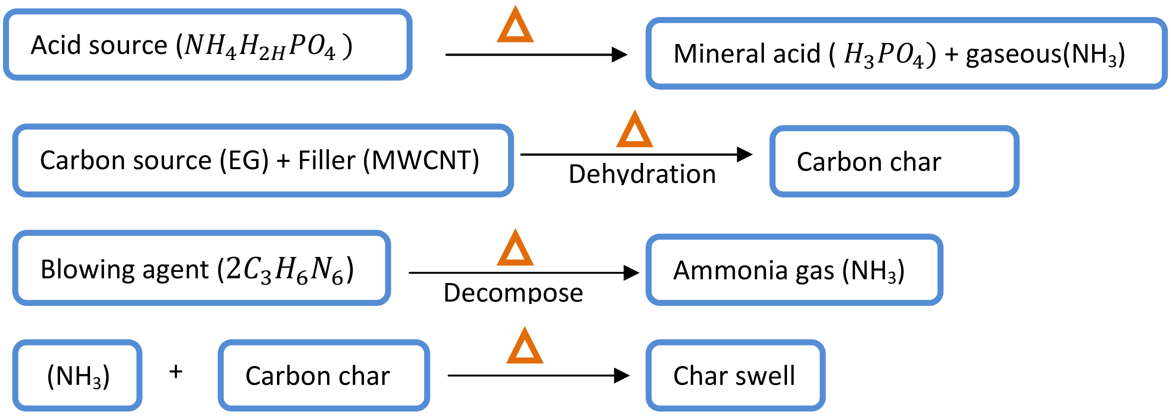


Figure 2.1: Chemical reaction of intumescent process

Chemical interaction between the "active" ingredient in the formulation lead to the formation of the intumescent char. It is generally accepted that first. The acid source breaks down to yield mineral acid, then it takes part in the dehydration of the carbonization source to yield the carbon char and finally the blowing agent decomposes to yield gaseous products. The latter cause the char to swell and produce the insulating multi-cellular protective layer. This protective char limits both the heat transfer from the heat source to the substrate and the mass transfer from the substrate to the heat source, resulting in conversation of the underlying material [M. Jimenez, S. Duquesne, S. Bourbigot, 2006].

In an ideal situation, intumescent can expand to around 100 times its original thickness. To achieve this requires careful selection of formulation components and carbon source and precise matching of processes involved.

2.1.1 Advantages of intumescent coating

- Intumescent coatings provide steel structures with corrosion protection, fire protection and a strong decorative element if required.
- Intumescent coatings are very lightweight
- Intumescent coatings are very easy to clean and maintain since they are relatively easy to apply.
- Intumescent coatings are fibre free so no dust

2.2. EXPANDABLE GRAPHITE

Expandable graphite [EG] is a low density carbon material having a series of unique properties: developed specific surface, binder-free pressing capacity, stability to aggressive media, and low thermal conductivity. **[I.M afanasov, D.V Savhenko, S.G. Ionov, D. A. Rusakov, A.N. Seleznev and V.V. Avdeed. thermal conductivity and mechanical properties of expanded graphite. Moscow State University, Russia. 2008].** EG is made by immersing natural flake graphite in a bath of chromic acid then concentrated sulfuric acid which forces the crystal lattice planes apart thus expanding the graphite. Under instant high temperature, the EG will expand and could stifle the flame when the fire broke. The expansion of the product leads to excellent oxidation resistance and temperature resistance. Because of the properties, it is used as fire retorted coating system and has a good synergist synergistic physical expansion of halogen flame retardants. When heated at certain extend, expandable graphite begin to expand, creating a very thick porous layer and a carbon layer to delay the termination of polymer layer.

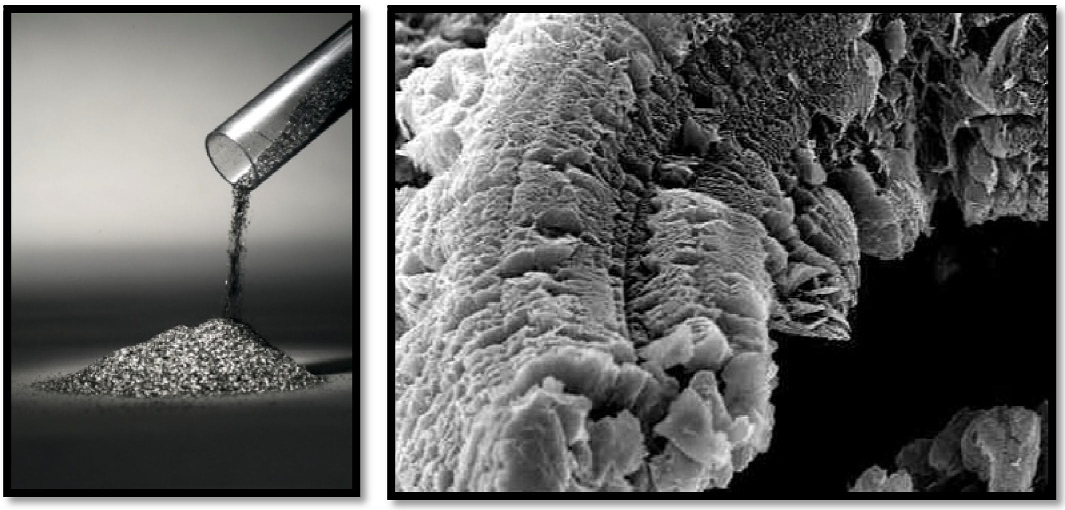


Figure 2.2: Expandable graph flake (left picture) and expandable graphite (right) with 10,000 times magnification

2.3. CARBON NANOTUBE

The discovery of carbon nanotube in 1991 marked the emergence of a new class of high performance polymer composites with nanotubes as the reinforcing material.

The exceptional mechanical and physical properties demonstrated by carbon nanotubes especially single wall carbon nanotubes, combined with their low density makes them an excellent candidates for composites reinforcement. These composites are being used to enhance the strength, stiffness and electrical conductivity.

Carbon nanotubes are fullerene – related structure which consists of grapheme cylinders closed at either end with caps containing pentagonal rings. [10]. generally the term "nanocomposites" describes as two phase material with as suitable nanofiller dispersed in a polymer matrix at the nanometer (10^9) scale. The ends of a nanotube might be capped with a hemisphere of the buckyball structure. Their name is derived from their size, since the diameter of a nanotube is on the order of a few nanometers (approximately 1/50,000th of the width of a human hair), while they can be up to several millimeters in length (as of 2008).

Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Structurally MWCNTs consist of multiple layers of graphite superimposed and rolled in on them to form a tubular shape. The MWCNT are the most reasonable ones for commercialization as composite addictive or coating elements. They offer less attractive properties, but they can be produced on high scale at a relatively low price.

Previous research has shown that nanoparticle fillers are highly attractive for the purpose of making a material more flame retardant, because they can simultaneously improve both the physical and flammability properties of the polymer nanocomposite. From perspective of Krzystof Grrzybowski in Potential application of carbon nanotube (CNTs) as a flame retardant additive technical and market analysis said that "Multi wall carbon nanotube are the most reasonable ones for commercialization as composite additive or coating element. They offer less attractive properties, but they can be produced on high scale at a relatively low price. In the past, their application area was limited to a few specific solutions, in which cost was not a driving factor (such as sport equipment). However, over the last two years, intensive scaling up of MWCNTs production has led to the dramatic price decrease down to below $100/kg (depending on the shipment condition)". This shown that the CNT can be

2.3.1. Application of CNT as addictive

Carbon Nanotubes are believed to be useful as flame retardant nanoaddictive because of their highly elongated shape and balance between the effect of thermal conductivity and shielding performance of external radiant flux (and heat feedback from the flame) at certain amount in a structural material [11]. Their excellent mechanical properties combined with their nano size and low density of 2.0 g/cm^3 makes them as viable reinforcing phase in a variety of polymer, ceramic and metallic matrices to design high-performance composite materials [12]. It is also believed CNT can provide innovative materials for thermal control application with their high thermal conductivity and high aspect ratios as well as the mechanical strength [13]. They also belief that the char form will be much denser.

Experiment conducted by Florentina Tutunea and Charles A. Wilkie from Department of chemistry, Marquette University on combination of carbon nanotubes with fire retardant material such as AHT (alumina trihydrate), DECA (decabromodiphnyl oxide), antimony oxide (Sb2O3) and resorcinol diphospate (RDP) conclude that there is interaction between ATH and the CNT which is manifested in a large amount if char and greatly decrease values of peak heat release. It is belief that there is some potential advantage in combining CNT with fire retardants in some polymers [14]

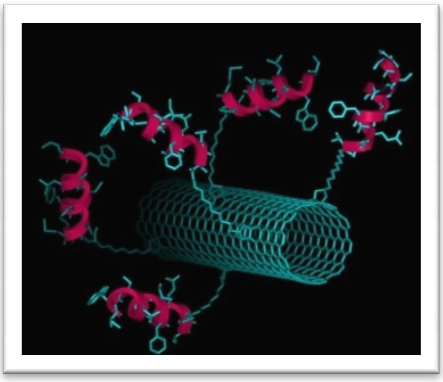
Some scientist has recently proposed application of CNTs in fiber composites. They found that the tensile strength of poly (vinyl alcohol) fill tripled with the addition of 1wt% of single wall nanotubes. According to the experiments, incorporation of 1wt% of CNTs in polyacrylonitrile increases the tensile strength and modulus of the resulting material by 64% and 49% actively. In Scientifics opinion the reinforce material reduced its shrinkage by 50% and possessed raised temperature of melting by 40˚C in comparison to the material without addictive. Moreover, mechanical analysis of CNTs based composites suggests that embedded particles may effectively hamper the formation of cracks that can propagate and lead to fatigue failure (Krzysztof Grzybowski, 2009).

Some of us wonder why using carbon nanotubes instead of other cheaper material such as clay and carbon nanofibers. It was found that these particles provide material nonflammability with relatively small concentration compared to other fillers. Carbon nanotubes usually possess diameters in the range from 50 to 150nm. CNT themselves are not flame retardants – they do not put out fire.

2.3.2. Advantage of MWCNT as carbon source

It is believed that MWCNT as carbon source in intumescent coating can have several advantages such as:

i. Provide a protective char on the material surface
    a. The char of CNT decrease the out of material diffusion of evaporated chemicals and simultaneously the diffusion of oxygen from closed environment toward the surface of the material.
    b. The char provided the heat thermal barrier – decrease heat rate of the heat transport. This will affect the melting of material and its evaporation by undergoes slower than in comparison to the unprotected one.
    c. The char produce will be much denser
ii. Boost mechanical strength (Up to15 to 20 times stronger than steel and 5 times lighter), thermal conductivity, electrostatic discharge features, electrical conductivity and thermal conductivity (same as that of diamond and are more than five times that of copper) – give significant impact on product performance and quality.
iii. Ignite more easily (increase time for the formation of char)
iv. Scaffold of carbon nanotubes causes that convective movement that appears during a fire in molten material is reduced and the relevant mass and heat transfer ratios are also decrease



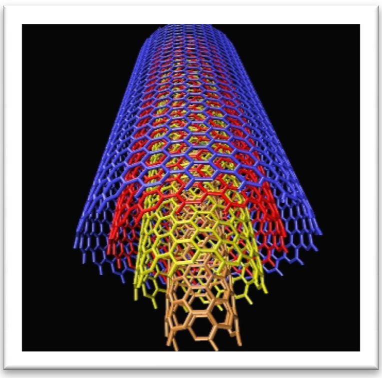


Figure 2.3: The bonding in carbon nanotubes is sp² (left) and Multiwalled carbon nanotube (MWCNT) model (right).

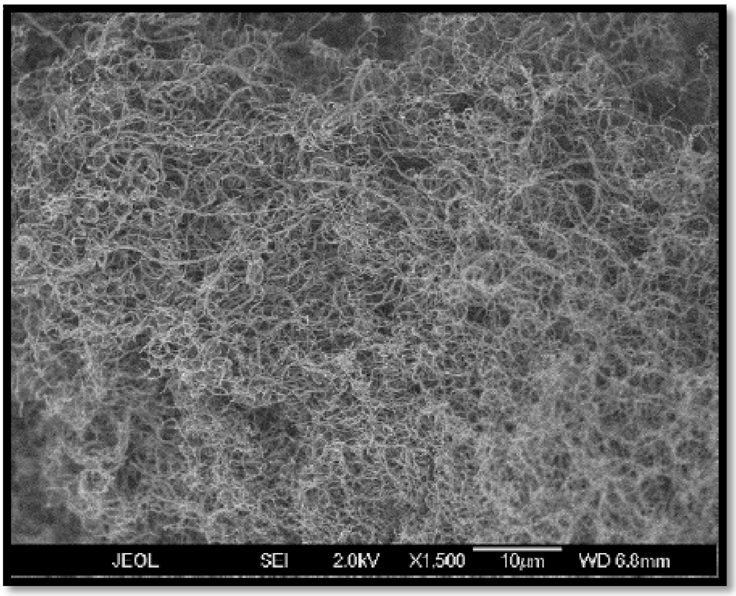


Figure 2.4: An example of carbon nanotubes in 1500 magnification

2.4. PROPERTIES OF SUBSTRATE (CARBON STRUCTURAL STEEL)

Carbon steel is by far the most widely used kind of steel. The properties of carbon steel depend primarily on the amount of carbon it contains. Most carbon steel has a carbon content of less than 1%. Carbon steel is made into a wide range of products, including structural beams, car bodies, kitchen appliances, and cans. In fact, there are 3 types of plain carbon steel and they are low carbon steel, medium carbon steel, high carbon steel, and as their names suggests all these types of plain carbon steel differs in the amount of carbon they contain.

The American Iron and Steel Institute (AISI) defines carbon steel as: "Steel is considered to be carbon steel when no minimum content is specified or required for chromium, cobalt, columbium, molybdenum, nickel, titanium, tungsten, vanadium or zirconium, or any other element to be added to obtain a desired alloying effect; when the specified minimum for copper does not exceed 0.40 percent; or when the maximum content specified for any of the following elements does not exceed the percentages noted: manganese 1.65, silicon 0.60, copper 0.60.

The grade for carbon structural steel used in this project is ZJ330B. The tensile strength for this steel is between 350 to 410 MPa. The composition in this steel is Carbon, Silica, Manganese, phosphorous and cooper [16].

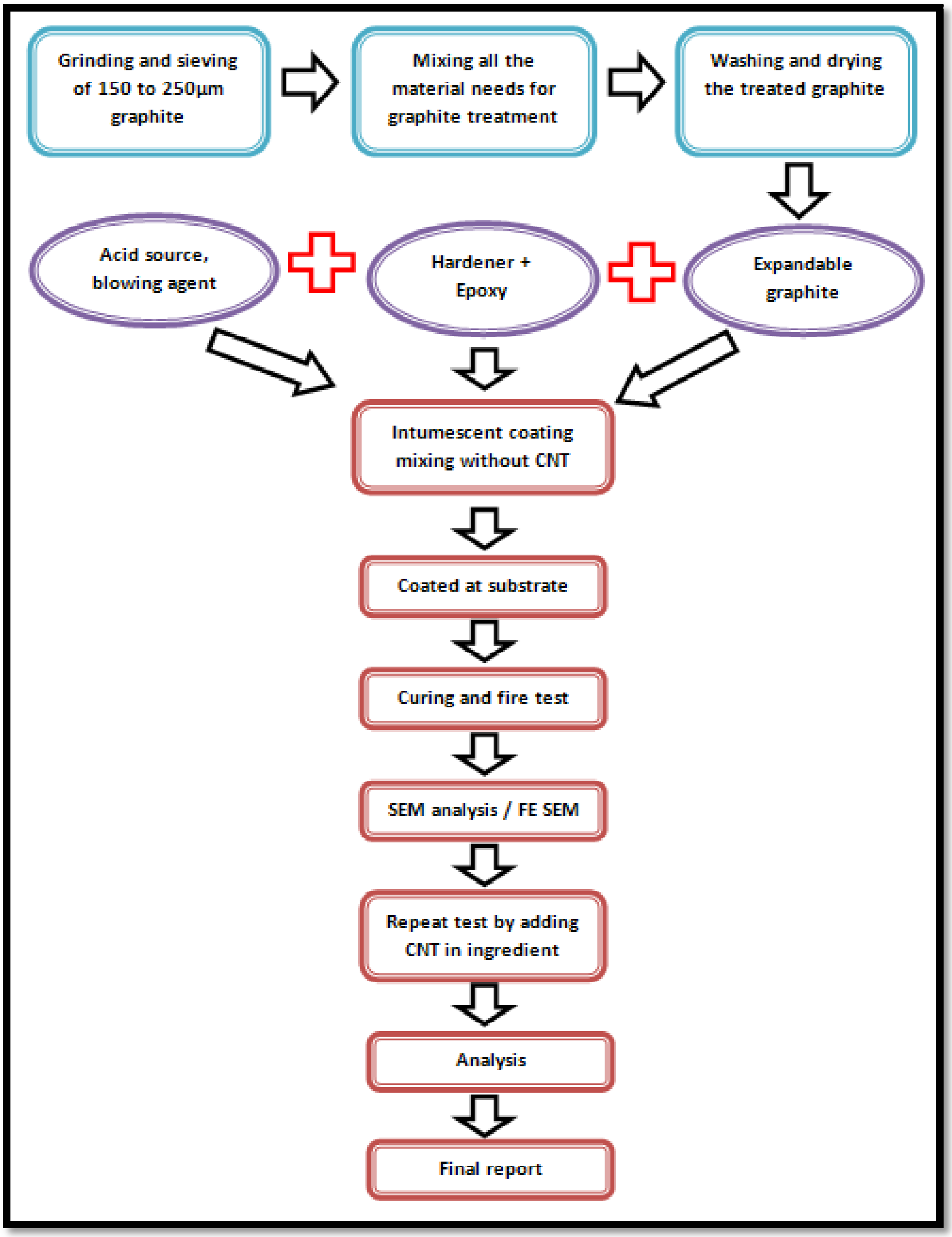
It is known that structural steel begins to soften around 425°C and loses about half of its strength at 650°C. This is why steel is stress relieved in this temperature range. (Thomas W. Eagar and Christopher Musso, 2001).

Figure 2.4: An example of structure steel use in building. Figure above showed the structure steel that support the academic building at Universiti Teknologi PETRONAS, Tronoh.

CHAPTER 3

METHODOLOGY

3.1. METHODOLOGY OF THE PROJECT



3.2. GANTT CHART FYP 1

Table 3.1: Gantt chart for final year project 1 (semester January 2010)

Activities	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
Selection of project topic + submission of proposal																
Research on selected topic																
Preparation and submission of preliminary report																
Project work : • Research on the literature review • Developed the intumescent formulation • Grind the graphite to smaller particle size • Sieve to 2 different size • Preparing the formulation for pre-experiment --treated graphite • Developed the expandable graphite								Mid Semester Break								
Submission of progress report																
Seminar																
Project work continue • Test and analysis of sample																
Submission of interim report final draft																
Oral presentation																

Earliest will be on 15th February and due on 17th February 2010 and end on 19th January

Earliest will be on 25th January and due on 28th January 2010 and end on 29th January

Earliest and due will be on 22nd March and end on 26th March 2010

Earliest and due will be on 3rd March and end on 7th May 2010

3.3. GANTT CHART FYP 2

Table 3.2: Gantt chart for final year project 2 (semester July 2010)

Activities	1	2	3	4	5	6	7		8	9	10	11	12	13	14
Project work Continue •Preparing intumescent coating using EG only •Furnace test •SEM test •Deciding the best formulation															
Submission of Progress Report I				▲											
Project work continues •Preparing for intumescent coating with CNT •Furnace Test															
Submission progress Report II									▲						
Seminar										▲					
Project work continues •SEM test •Thermoanalysis •Compared and Analyze															
Poster Exhibition												▲			
Submission of Dissertation Final Draft															
Oral Presentation															
Submission of Dissertation (hardbound)															

▲ Earliest will be on 16th and due on 20th August 2010
▲ Earliest will be on 20th and due on 24th September2010
▲ Earliest will be on 20th September and end on 1st October 2010
▲ Earliest and due will be on 11 and end on 15th October 2010

3.4. MATERIAL SELECTION

3.4.1. Expandable graphite

i. Graphite
ii. Acetic acid
iii. Sulfuric acid
iv. Potassium Permanganate ($KMNO_4$)

3.4.2. Intumescent Coating

v. Expandable graphite
vi. Carbon nanotube
vii. Ammonium Polyphosphate (APP)
viii. Melamine
ix. Triethylenetetramine (TETA) and epoxy *as binder*
x. Boric Acid - Combination of boric acid and APP will provide a better performance of intumescent coating when they are separately incorporated into a resin.

3.5. PROCEDURE

3.5.1. Pre-Experiment – treated graphite (expandable graphite)

i. The graphite need to be grind by using grinder to get smaller particle size
ii. Sieve the graphite to have smaller particle size 150 µm
iii. Using the formulation of expandable graphite (all formulation are same for all particle size) as follow

Table 3.3: Treated graphite formulation

Sample	Graphite (%)	Acetic acid (%)	Sulfuric acid (%)	Potassium Permanganate (%)
1	28	56	14	2

Tool

Three neck around bottom flask, Magnetic stirrer, Hot plate, Thermometer, Reflux condenser, pipette, dropper, beaker, spatula, bowl, and container

Material

Graphite, Acetic acid (CH_3COOH),, Sulfuric acid(H_2SO_4), Potassium Permanganate ($KMNO_4$) and distilled water

Arrange the equipment as follow:

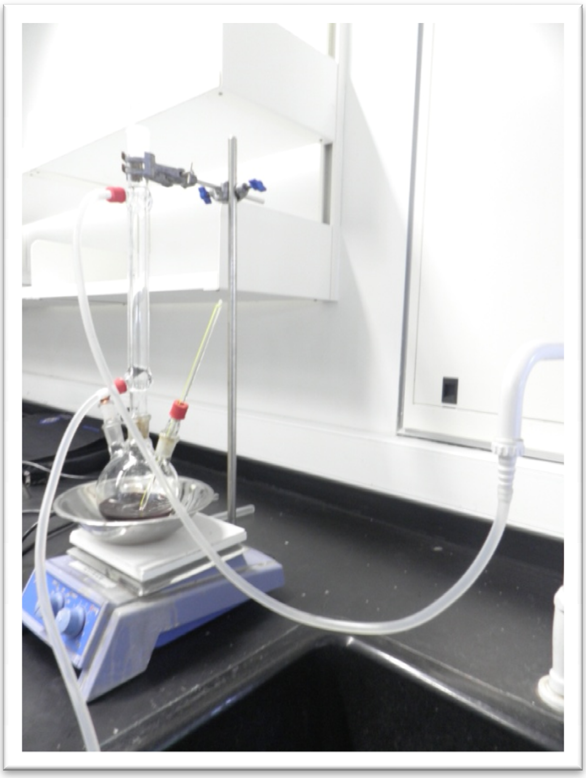


Figure 3.1: Arrangement of equipment for the preparation of expandable graphite

1. Prepare the 150 μm graphite for 50g and pour the graphite into three necks around bottom flask.
2. Prepared the Potassium Permanganate for 3.5g and pour into three neck around bottom flask
3. Put the magnet into the three necks round bottom flask and set the hot plate with 2.5 -3rpm speed

4. Then, pour the Acetic Acid into the flask.
5. Check the temperature of the mixture by using thermometer
   Note: The temperature should maintained at room temperature (26˚C)

6. Connect the small tube through the pipe into the top hole of the condenser and the other tube is connected to the sink from the bottom hole of the condenser.
7. Open the pipe to make the water flow through the condenser and maintained at room temperature (26˚C).
8. Prepared the sulfuric acid (25g) and slowly drop Sulfuric Acid using dropper into the three necks round bottom flask.
   Note: The sulfuric acid must be slowly dropped to avoid temperature increase rapidly.

9. Leave the graphite to be mix for one hour
10. After 1 hour, wash the mixture by using distilled water until it colorless.
11. Finally, put the mixture into the oven for 3 hours at 60^0C to dry it. Below is the chronology picture during the preparation.

Preparation for Expandable Graphite

Figure 3.2: Graphite before it been grind

Figure 3.3: The grinder machine use to grind the graphite to smaller particle size

Figure 3.4: Tighten the machine to ensure the graphite will be waste

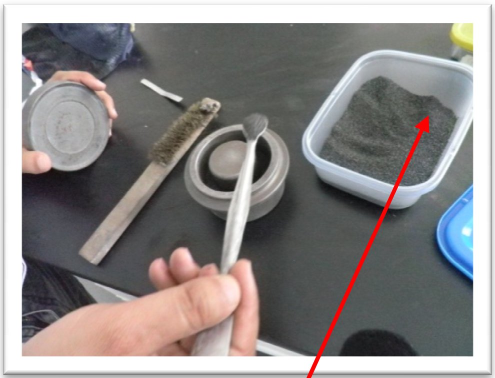


Figure 3.5: graphite after grinded

Figure 3.6: Graphite being sieve using 150 µm size

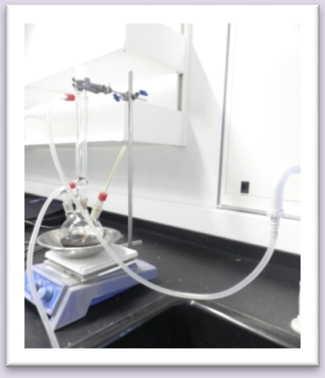


Figure 3.7: Equipment preparation for graphite treatment.

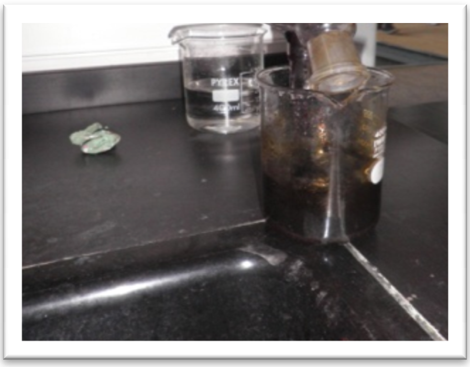


Figure 3.8: The treated graphite was using distilled water until it colorless.

Figure 3.9: heating the expandable graphite in oven for 3hour to dry it

3.5.2. Preparation of Intumescent Coating

A total of 13 formulations were developed without CNTs as a bench mark while a total of 15 formulations reinforced with CNTs were developed and will be compared in analysis.

Equipment used

Containers, Mixture, small spoon

Material used

Expandable Graphite, Ammonium Polyphosphate (APP), Melamine, Boric Acid, Bisphenol A (BPA), Triethylenetetramine (TETA), carbon steel

General Procedure:

1. Weight the Ammonium Polyphosphate (APP), Melamine and Boric Acid using the formulation developed.
2. Grind the 3 ingredient in grinder for 30 second.
3. Weight the expandable graphite and mix it with the ingredient that already grinded.
4. Put the Bisphenol a (BPA) and Triethylenetetramine (TETA) into container by using spoon and mix well using mixture for 40-50rpm in 15 minutes.
5. Using spoon, carefully pour the mixing ingredient early and stir the mixture in container with epoxy and hardener using 12rpm for 5 minutes before increase the speed.
6. Apply the coating at the surface of carbon steel. Cover it smoothly and homogenously.
7. Leave it on for two weeks for curing.

3.6. EQUIPMENT USE FOR ANALYSIS

Analysis of performance and characteristics of the sample of intumescent coating can be done using the listed machine as below:

i. SEM (*scanning electron microscope)*

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today. The SEM can produce very high-resolution images of a sample surface, revealing details about 1 to 5 nm in size.

Figure 3.10: An example of SEM equipment

ii. XRD (*X-ray diffraction*)

X-ray diffraction finds the geometry or shape of a molecule using X-rays. X-ray diffraction techniques are based on the elastic scattering of X-rays from structures that have long range order. Powder diffraction (XRD) is a technique used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. It is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data.

Figure 3.11: Example of XRD (left) and FE SEM machine (right)

iii. FE SEM (*Field Emission Scanning Electron Microscope*)

A field-emission cathode in the electron gun of a scanning electronmicroscope provides narrower probing beams at low as well as high electronenergy, resulting in both improved spatial resolution and minimized samplecharging and damage. FESEM produces clearer, less electrostatically distorted images withspatial resolution down to 1 1/2 nm. That's 3 to 6 times better than conventional SEM **(PhotoMetrics, Inc.).**

3.7 FIRE TEST

3.5.1 Bunsen burner

This test has been used to characterize some properties of the char. A high temperature (more than 1000˚C) is applied with a Bunsen burner on to intumescent coating. Steel started to loses it properties at around 500˚C. Because of this, and because a thermocouple is used at the back of steel plate, a 450˚C is chosen as failure temperature. The test will conduct to determine the temperature that reach the substrate (steel) when fire direct coating. This test will allow us to decide the ability of the coating to slow down and prevent the heat from reaching the substrate.

Figure 3.12: Bunsen burner test and setup equipments

3.5.2 Furnace

Three different types of temperature are used for furnace test. The temperature are at 400, 500 and at 600˚C. The temperature at 400˚C is used to determine the ignition rate of the coating, the 450˚C is the temperature used to see the characteristic of the char and for 600˚C to see the strength of the char to maintain the inflammable properties for more than 4 hours.

Figure 3.13: Furnace used in this experiment

CHAPTER 4
RESULT AND DISCUSSION

4.1 INITIAL RESULT - FORMULATION OF THE INTUMESCENT COATING SAMPLES WITHOUT CARBON NANOTUBES

A total 13 formulation were produced in early stage of the project using 150 µm size for graphite. The formulations were produced based from resources in the journal, books and with a help of post graduate students having experience in intumescent process. The 13th formulations are produced by varies the weight percentage of carbon source, acid source and blowing agent. Constant value was used in binder. Five samples were developed using each formulation. The sample will be used in fire testing later. 4 best samples were chosen by physical observation by looking at the characteristic of the char strength such as the smooth surface and ability to maintain at temperature 450˚C.

4.1.1 Steps in developed intumescent coating without carbon nanotubes

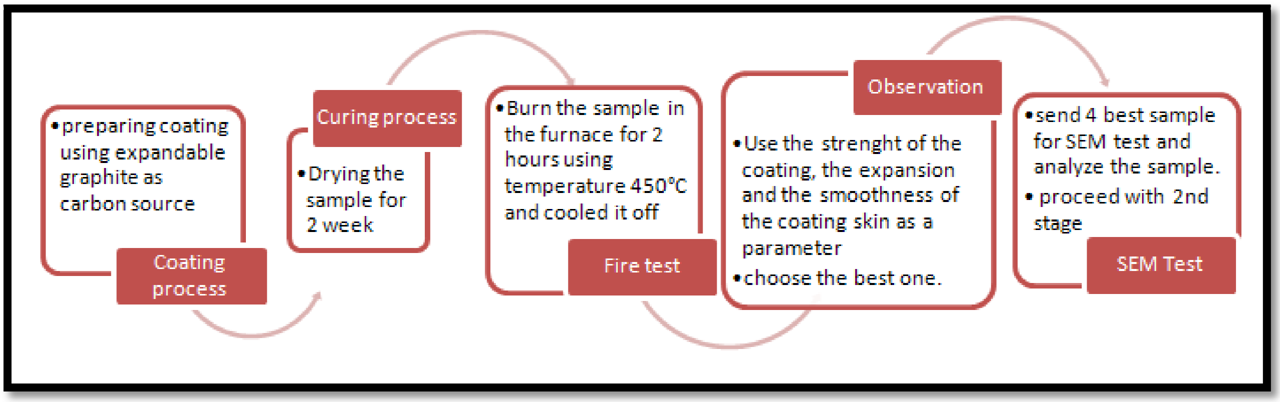
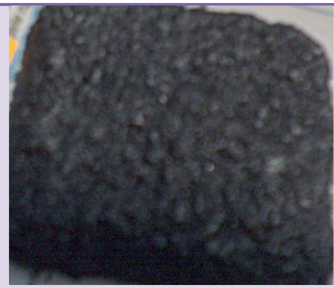
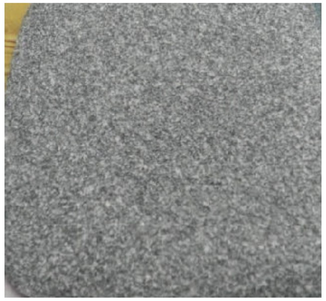
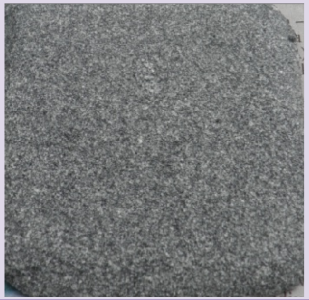
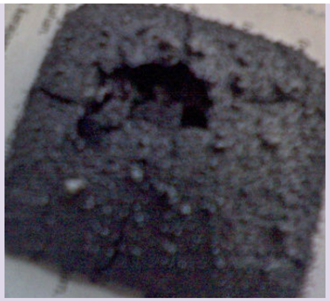


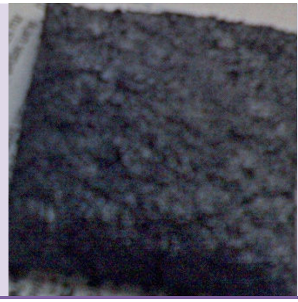
Table 4.1: Bench mark formulation for intumescent coating without carbon nanotubes

Sample name	Expandable Graphite (g)	APP (g)	Melamine (g)	Boric acid (g)	Epoxy (g)	Hardener/binder (g)
D21	5	10	10	5	40	20
D22	5	10	7.5	7.5	40	20
D23	5	10	5	10	40	20
D24	5	7.5	10	7.5	40	20
D25	5	5	10	10	40	20
D26	7.5	10	7.5	5	40	20
D27	10	10	5	5	40	20
D28	7.5	7.5	10	5	40	20
D29	10	5	10	5	40	20
D30	7.5	7.5	7.5	7.5	40	20
D31	5	7.5	7.5	10	40	20
D32	10	7.5	7.5	5	40	20
D33	7.5	10	5	7.5	40	20
Percent	33.33%				66.67%	

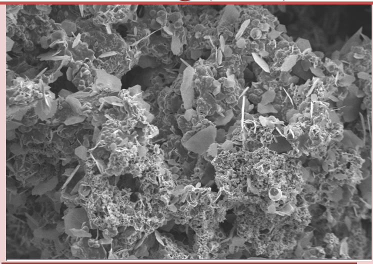
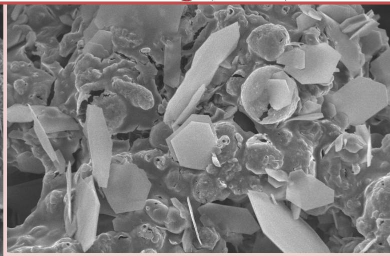
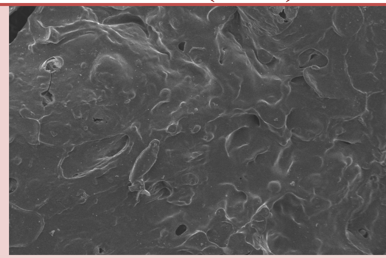
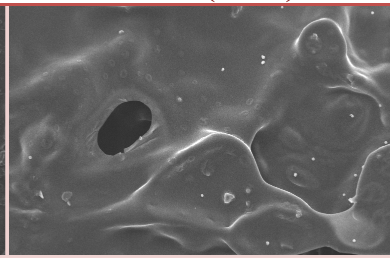
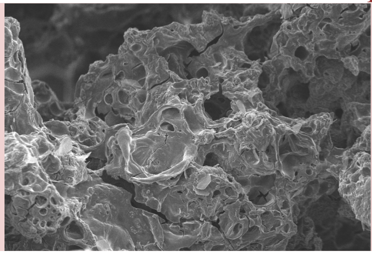
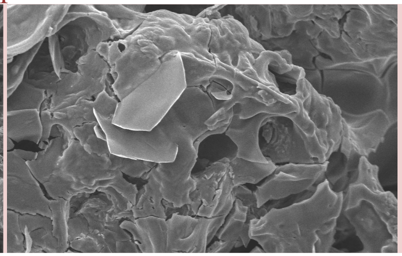
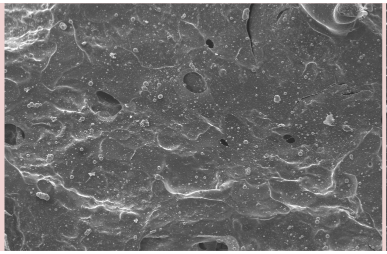
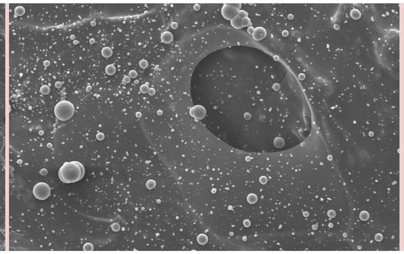
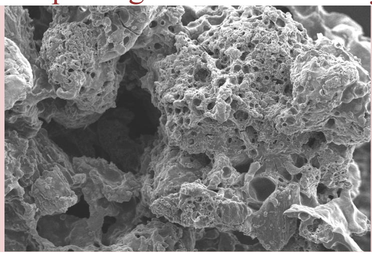
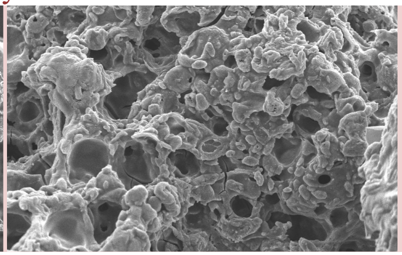
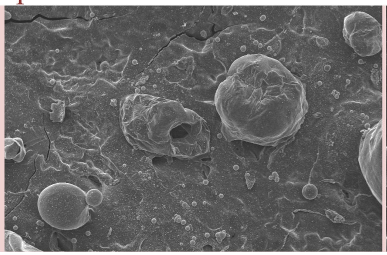
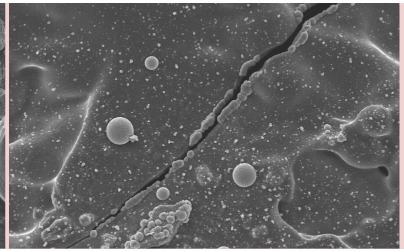
**Highlighted is the best sample obtain based on physical observation. Because of limited time and resources, only 4 samples were send for SEM test which are D23, D26, D27and D28*

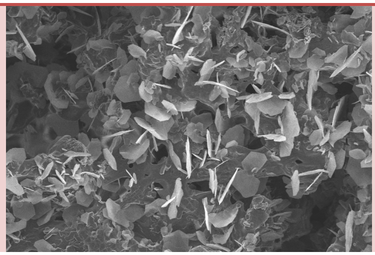
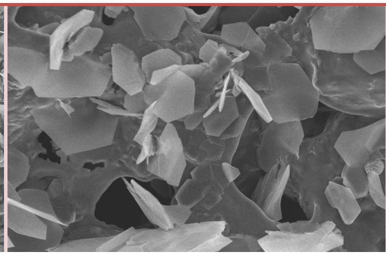
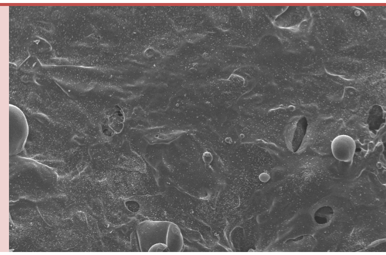
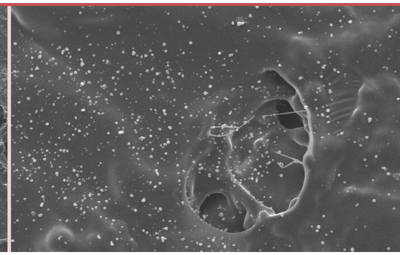
4.1.2 Result of sample without CNT after undergo furnace test at 400˚C

Sample name	Coating before fire test	Coating Thickness (mm)	After place in furnace	Expand thickness (mm)	Observation
D23		3.75		13.6	• 2.63 times expanded from original size. • The coating is harder and skin is rough after place in furnace • Really strong attach to the substrate
D26		3.06		18.5	• 5.05 times expand from original size • the skin is bit rough but the expand time is higher compared to other sample • bubble build up the surface coating
D27		2.95		13.1	• 3.44 times expand from original size • The surface is rough • The skin is too smooth. It break when touch • There is little crack and some bubble build up at the surface area

D28		3		10	• 2.33 times expand from original size • Skin smooth • Expansion is not well • The coating inside is hard/stronger compare to the skin.
D33		3.14		10.28	• 2.31 times expand from original size • Skin not too smooth • Expand a little

4.1.3. Analysis of SEM Result – the sample were send after the fire test using furnace

Sample name	Inside coating (100X)	Inside coating (500X)	Outside - skin (100X)	Outside - skin (500X)
D23				
	The SEM result indicate that lot of flakes exist in the sample. This shown that the mixture process is not well done.		The skin is little smooth and no buble build up at the surface. Several hole were found on the skin.	
D26				
	The mixture of the material is fine. The texture inside the sample is good. Not too many flakes found in the mixture.		Rough skin but little hole found in skin. A lot of bubble builds up at the surface.	
D27				
	Good texture inside the sample. The expansion is well spread.		Rough skin. Bubble can be seen at 100 times magnification. A long crack exists at the surface.	

D28	  Mixture is not done too well. Flakes build up inside the coating and the material is not well expand.	  Surface is nearly smooht but little hole exist at the surface.

4.2. FINAL FORMULATION OF THE INTUMESCENT COATING SAMPLES WITH CARBON NANOTUBES

4.2.1 Steps in developed intumescent coating with carbon nanotubes

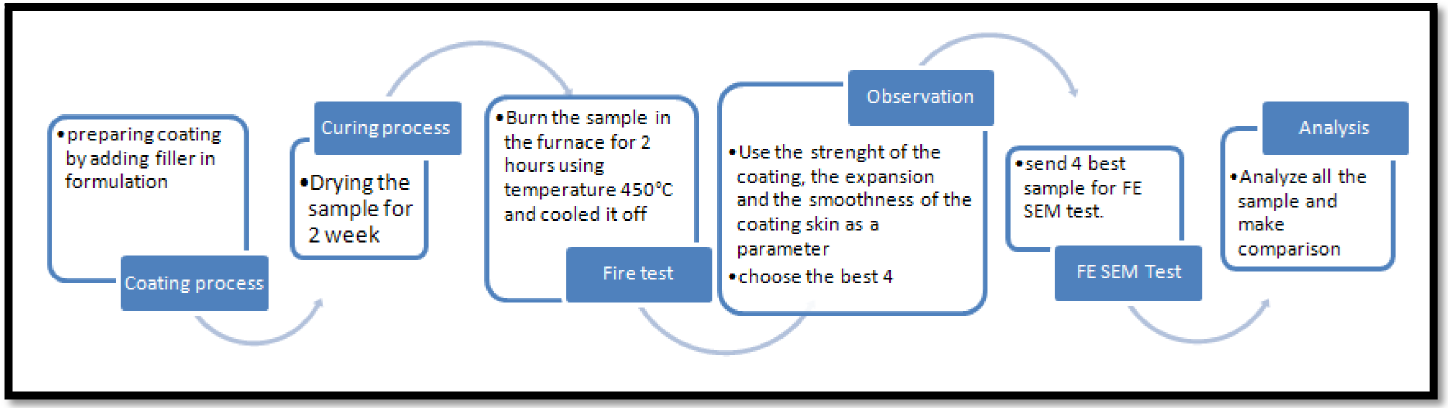


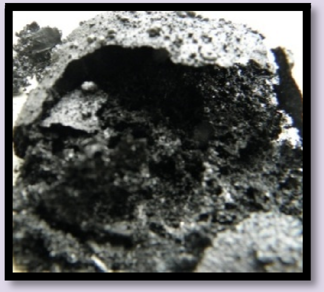
Table 4.2: Final formulation of intumescent coating with carbon nanotube

Sample name	Expandable graphite	CNT	APP (g)	Melamine	Boric Acid	Epoxy	Hardener/binder
NA23	4.82	0.18	10	5	10	40	20
NB23	4.73	0.27	10	5	10	40	20
NC23	4.64	0.36	10	5	10	40	20
NA26	7.32	0.18	10	7.5	5	40	20
NB26	7.23	0.27	10	7.5	5	40	20
NC26	7.14	0.36	10	7.5	5	40	20
NA27	9.82	0.18	10	5	5	40	20
NB27	9.73	0.27	10	5	5	40	20
NC27	9.64	0.36	10	5	5	40	20
NA28	7.32	0.18	7.5	10	5	40	20
NB28	7.23	0.27	7.5	10	5	40	20
NC28	7.14	0.36	7.5	10	5	40	20
NA33	7.32	0.18	10	5	7.5	40	20
NB33	7.23	0.27	10	5	7.5	40	20
NC33	7.14	0.36	10	5	7.5	40	20
Percent			33%				66.67%

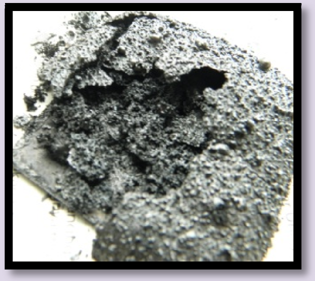
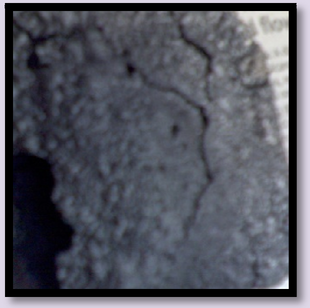
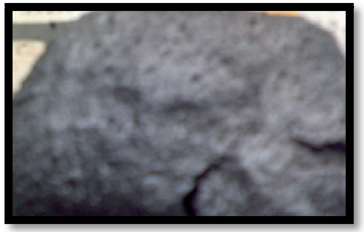
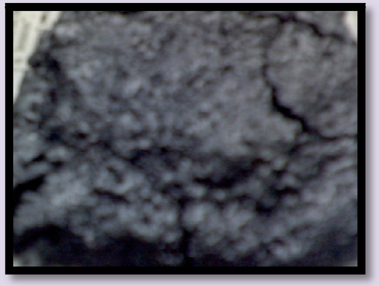
In this Final stage of formulation, a total of 15 formulations were developed. During these stages, 2 types of fire test are used to analyze the sample. All the samples were undergoing furnace test at 450˚C but only several were selected to test at 600˚C. The best 4 sample then were chosen and are then send for FE SEM analysis. The same formulation used in Bunsen burner test and will be compared with sample without adding CNT. A chart and graph then produced to show the analysis.

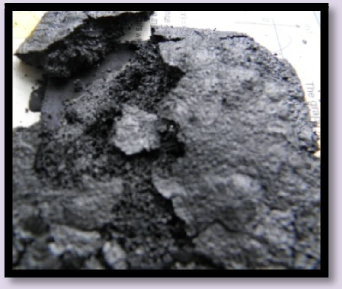
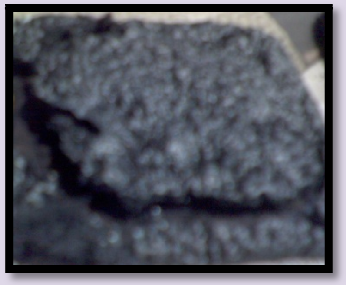
4.2.2 Comparison analysis after furnace test at 450˚C

Formulation without filler (D23)	Formulation Name	Formulation with filler (CNT) N23	CNT Expansion percent from real size	Net Expansion (%Adding filler – %without filler)	Comparison
Outside 	NA23		572%	117%	• Inside of coating is full (much denser compared without adding filler) • The skin is not brittle. Like there some shine skin layer cover the coating.
Inside 	NB23		748%	184%	• Same as NA23, the inside of the coating is full indicating the theory true. But the skin show crack and not glow as the NA23. • The expansion is high
• 263% times expanded from original size. • The coating is harder and skin is rough after place in furnace • Really strong attach to the substrate	NC23		747%	184%	• The expansion is high. • The skin glow. Some sort of ductile layer appears at the skin. • The expansion is higher compare to without filler. • The sample fracture easily when touch. Maybe due to the mixture during the coating is not done well.

Formulation without filler (D26)	Formulation Name	Formulation with Filler (CNT) N26	CNT Expansion percent from real size	Net Expansion (%Adding filler – %without filler)	Comparison
Outside  **Inside**  • 505% times expand from original size • the skin is bit rough but the expand time is higher compared to other sample • bubble build up the surface coating	NA26		682%	35%	• The skin is shining compared to D26 and more smooth. • Coating inside full. All the mixture and react well. • No crack exists.
	NB26		260%	-59%	• No expansion. Maybe due to the coating not apply well to the steel. • The skin is not brittle. • Crack occurred.
	NC26		822%	62%	• No crack appears. • The coating got good attachment to the steel substrate. • The inside coating is not full.

<table>
<tr><th>Formulation without filler (D27)</th><th>Formulation Name</th><th>Formulation with Filler (N27)</th><th>CNT Expansion percent from real size</th><th>Net Expansion (%Adding filler – %without filler)</th><th>Comparison</th></tr>
<tr><td rowspan="3"><u>Outside</u>

<u>Inside</u>

• 344% times expand from original size
• The surface is rough
• The skin is too smooth. It break when touch
• There is little crack and some bubble build up at the surface area</td><td>NA27</td><td></td><td>384%</td><td>11%</td><td>• Slight increase in expansion
• Crack still occurred
• The skin is not brittle
• Inside hard indicate good reaction of filler</td></tr>
<tr><td>NB27</td><td></td><td>754%</td><td>119%</td><td>• Good expansion
• Crack occurred at the edge of sample maybe due to the coating not apply well
• The skin is smooth and hard
• Inside is full.</td></tr>
<tr><td>NC27</td><td></td><td>434%</td><td>26%</td><td>• The coating is not well expanding.
• Crack occurred at the sample
• The skin not smooth. The sample might need to be test using furnace again.</td></tr>
</table>

Formulation without filler (D28)	Formulation Name	Formulation with Filler (N28)	CNT Expansion percent from real size	Net Expansion (%Adding filler – %without filler)	Comparison
Outside  **Inside**  - 233% times expand from original size - Skin smooth - Expansion is not well - The coating inside is hard/stronger compare to the skin.	NA28		651%	179%	The Skin brittle Inside coating full and hard (good result) The net expansion is quiet well
	NB28		555%	138%	Not good sample Even though it expand, the crack occurred from the middle of the sample The formulation might need to be test again
	NC28		346%	48%	Not good sample. Slight expansion but the sample having big crack. maybe need to redo the furnace test to see the real problem occurred.

4.2.3 FE SEM analysis for sample adding carbon nanotube

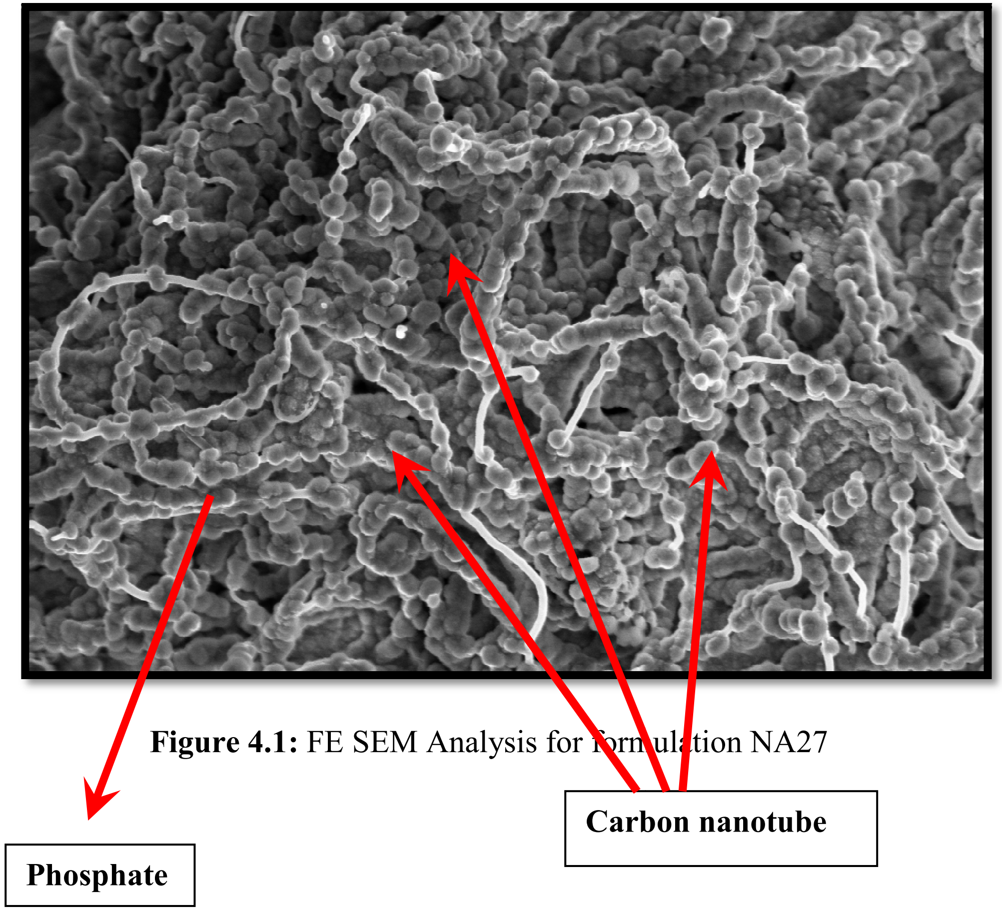


Figure 4.1: FE SEM Analysis for formulation NA27

SEM Analysis left showed the good bond of carbon nanotube with the other material to form the denser char. The small diameter of nanotube help in improved the char strength at higher temperature. A good bonding between CNT and phosphate can be seen at left picture. This help in increase ignition time of the sample when a fire occurred. The scaffold of CNT causes that convective movement that appear during fire molten material is reduced and the relevant mass and heat transfer ration are also decreases.

4.2.4 Fire test using furnace at 600˚C

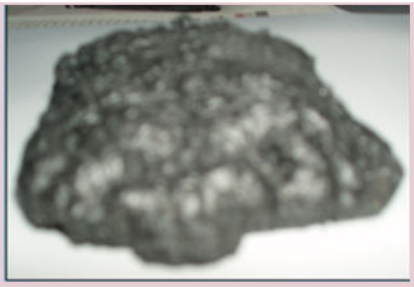
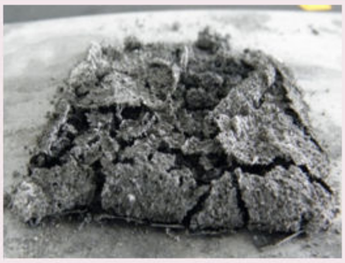
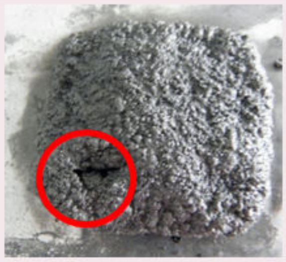
Formulation	27	23
With CNT		
Without CNT		

Figure above shown the crack at the sample without the CNT which indicate high release rate at the coating when temperature reach 600°C compared to with CNT where char still in good shape. When a CNT added in the formulation, a crack is reduced and this has shown in the FE SEM result earlier.

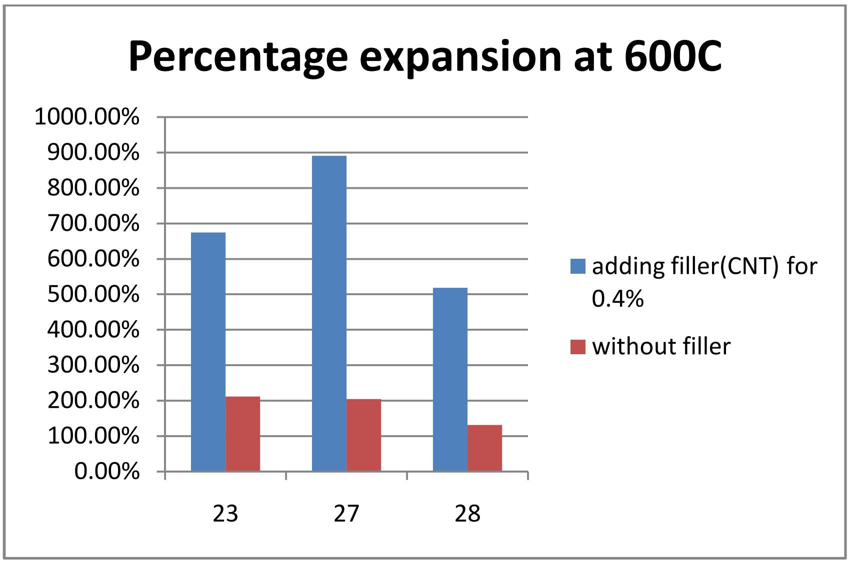


Figure 4.2: Percentage expansion chart at 600˚C

The chart above shown that, CNT has a high expansion at temperature 600°C for more than 4 hours. This result proved the theory [2] that CNT will reduce the heat release rate since no crack was form as the picture above.

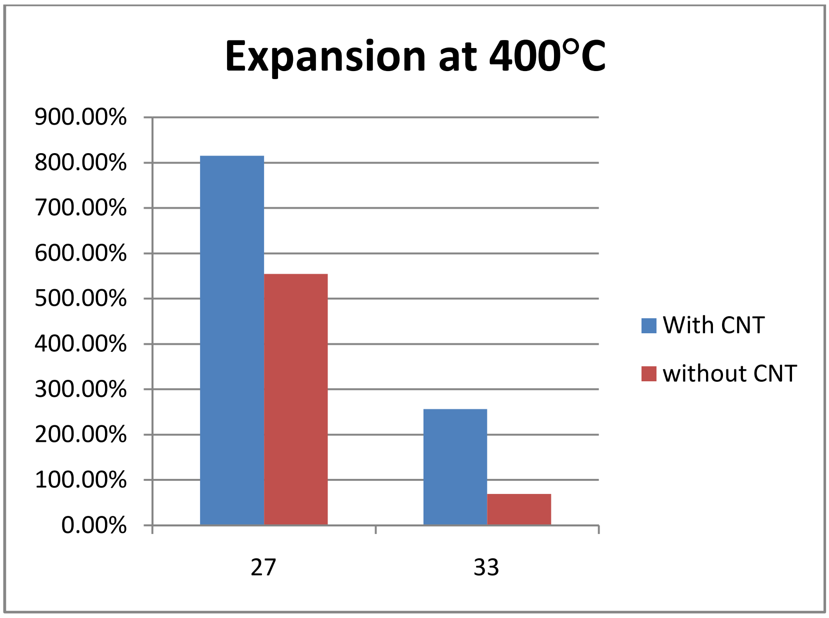


Figure 4.3: Expansion at 400˚C

The chart shown that the reinforce material (CNT) ignite more easily since the expansion for the CNT sample increase higher compare without adding filler at temperature 400°C for more than 2 hours. The result proved the theory by adding CNT will boost up the ignition rate of the intumescent material.

4.2.5 Bunsen burner Test

2 types of formulations are used for this type of test. The test is done for 1 hours and 450˚C is used as indication of failure of the coating. A direct fire by Bunsen burner can reach more than 1000˚C in just few minutes. A thermocouple is attached at the back steel of the substrate to measure the temperature of the steel when a direct fire occurred and proving the theory. As shown below, a remarkable things occurred when an addictive were added in the formulation.

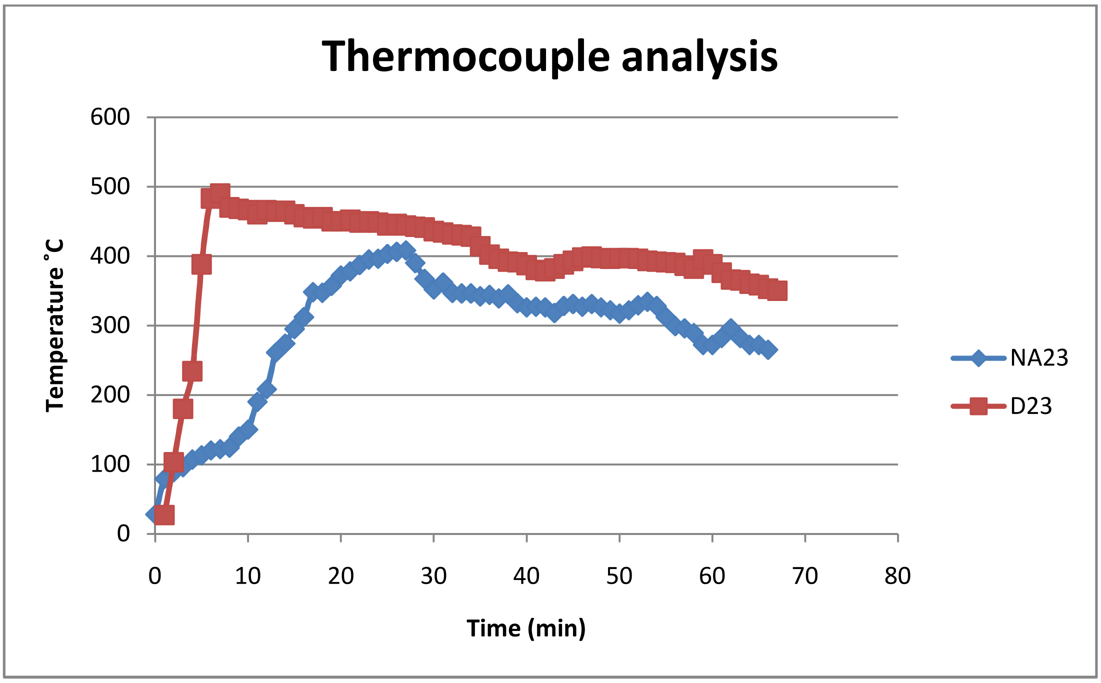


Figure 4.4: Thermocouple analysis for formulation 23

The above graph had shown the thermocouple analysis done for formulation 23. For sample without CNT, the slow process for the coating to fully work will lead to failure since the sample reach more than 450˚C – a temperature of failure in this project. Even though the temperature of the coating decreases back, the chance of the temperature reach more than 500˚C at the structure steel is high in real life. By adding CNT, the ignition rate boost up and at 400˚C, the coating properties to protect the structure steel already started doing a good job. This is shown since the temperature start decreases at minute 27.

Figure 4.5: A sample coating for formulation 23 after Bunsen burner test. At the left is formulation for NA23 and at the right is D23.

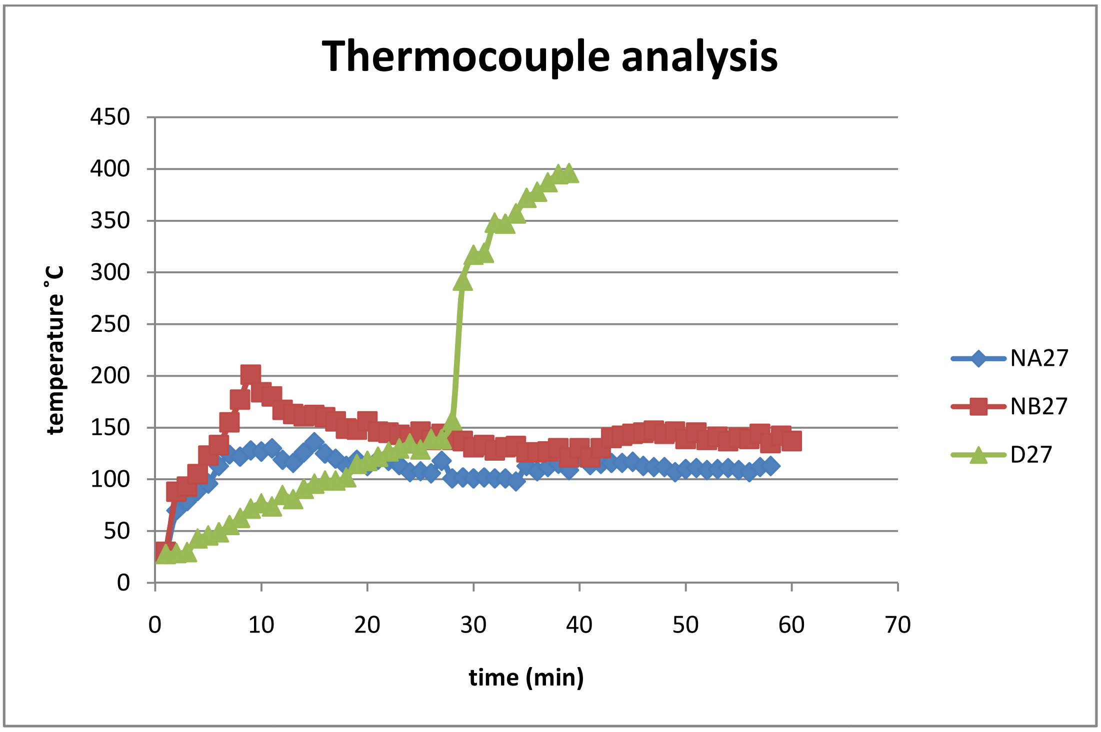


Figure 4.6: Thermocouple analysis for formulation 27

When the experiment done for formulation 27, the Bunsen burner is set to half open compared to sample 23. This to avoid the damage at the thermocouple since temperature of Bunsen burner may reach to 1000˚C. During the time, a sample with carbon nanotubes has shown remarkable results as compared to sample without carbon nanotubes. When adding CNT, both samples had shown lower working temperature compared to sample without CNT. The samples without CNT (D27) couldn't sustain longer in the experiment since a hole exist after 40 minutes. This concludes the failure for the sample to maintain as a protection to structure steel when a direct fire occurred at the structure steel.

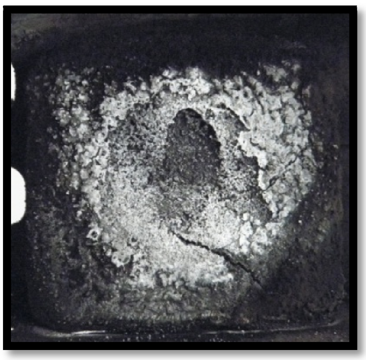


Figure 4.7: A sample coating for D27 after Bunsen burner test

CHAPTER 5

CONCLUSION AND RECOMENDATION

5.1. CONCLUSION

As describe earlier, the intumescent coating generally contain three active ingredients together with binder (Triethylenetetramine (TETA)*)* which is acid source (ammonium polyphosphate), a carbon source (carbon nanotube and/or expandable graphite) and blowing agent (melamine). Intumescent coating represents an important class of passive fire-proofing materials, which concern insulating systems designed to decrease heat transfer from a fire to the substrate being protected. They appear similar to a paint finish, and remain stable at ambient temperature.

However, in case of fire, coating expand to many times their original thickness, which result in the formation of insulating foam-like layer or 'char' which protect the steel. The char reduces the rate of heating of the steel and hence prolongs its load bearing capacity. As the temperature rises the binder begins to melt and the blowing agent liberates gases causing a controlled expansion. At the same time there is degradation of the carbon backbone and fusion of the inorganic reinforcing materials, resulting in char solidification [9].

A total of 13 formulations were developed without CNTs and tested for expansion and char strength. Based the results, a set of 4 formulations were selected for reinforcing CNTs. A total of 15 formulations reinforced with CNTs were developed. The formulation is developed by varying the percentage of CNT. Fire test and SEM were done to analyze the char strength and microstructure of char. The char expansion achieved was approximately 9 times and microstructure showed good bonding of CNT within the char.

Adding carbon nanotube in the intumescent coating will increase the ignition rate and improved the thermal properties. This is proved when a Bunsen burner test was conducted on the sample. Different composition of intumescent materials will give different type intumescent behaviour. An increase in blowing agent – melamine will increase the expansion times of the char while adding more CNT will boost the char strength. The best formulation is the formulation that balances all the composition and this shown in formulation 23.

5.2 RECOMENDATION

There are some recommendation in order to improve the quality of this study and the quality of the intumescent coating itself. Below are several recommendations that have been suggested by the author:

The samples should undergo TGA (thermogravimetric) analysis to better understanding in thermal conductivity of the sample.

A more analysis recommended to be done for all samples to see the boosting effect by adding carbon nanotube as addictive. A test to evaluate the denser of the char should be perform to proved more about the increment in the char strength as stated in the theory.

During the experimental work was performed, the fire testing conducted are not following the ASTM standard as UTP do not have the facilities as stated in the ASTM Standard. Complete facilities should be provided by UTP to ensure fire testing can give a more accurate result.

During analysis, only 4 samples can be sent for SEM analysis per month. This gives limitation for the author to do analysis for all the samples provided. SEM machines should be added more in UTP students need to wait to finish their analysis when a machine broken.

A research should be done using various size of expandable graphite. The diameter of particle had effect in the performance of the intumescent fire retardant material as shown by carbon nanotubes.

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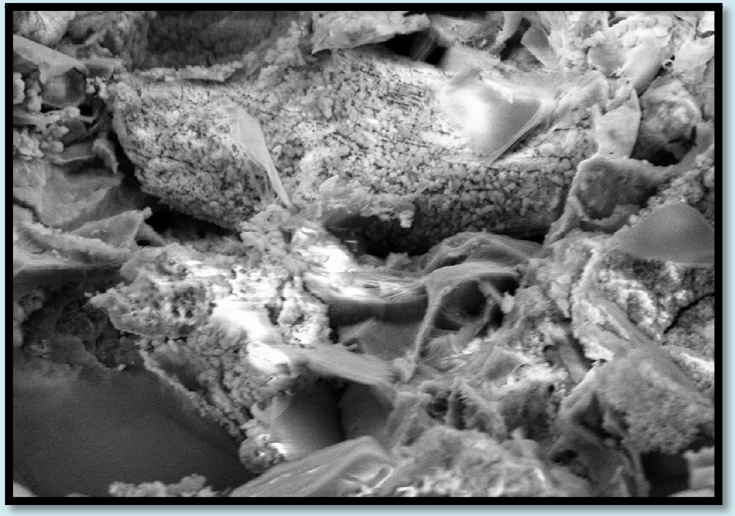
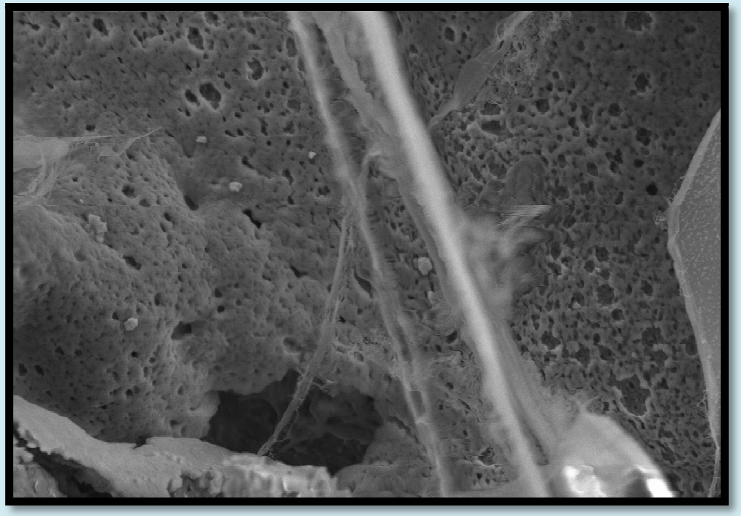
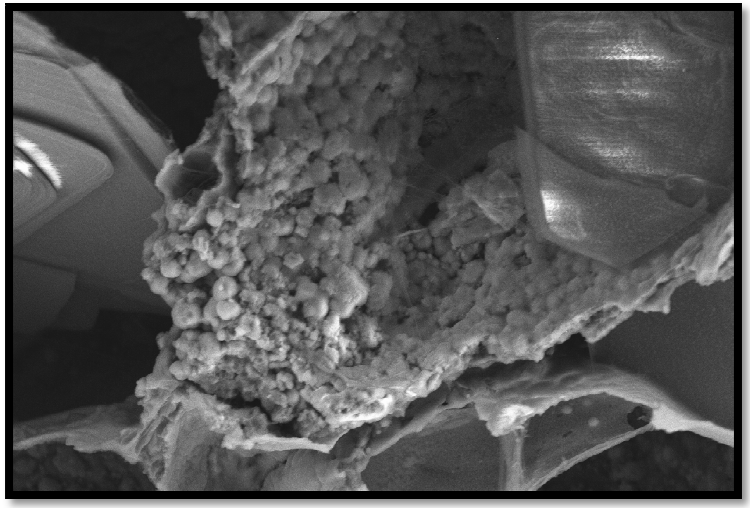
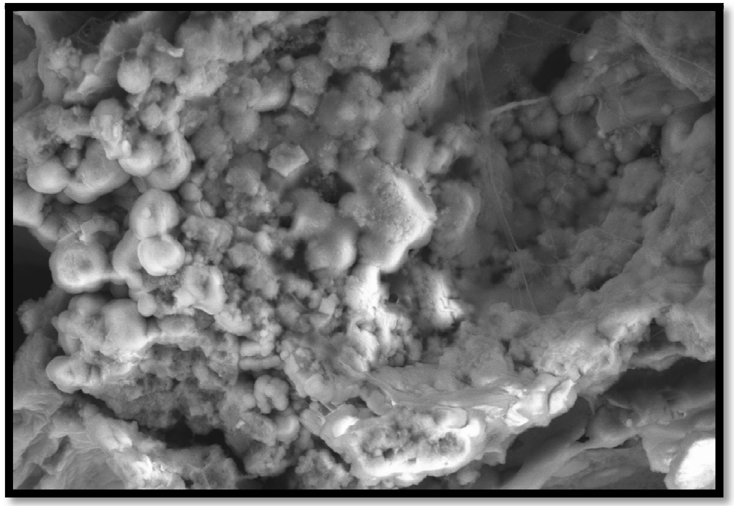
APPENDIXES

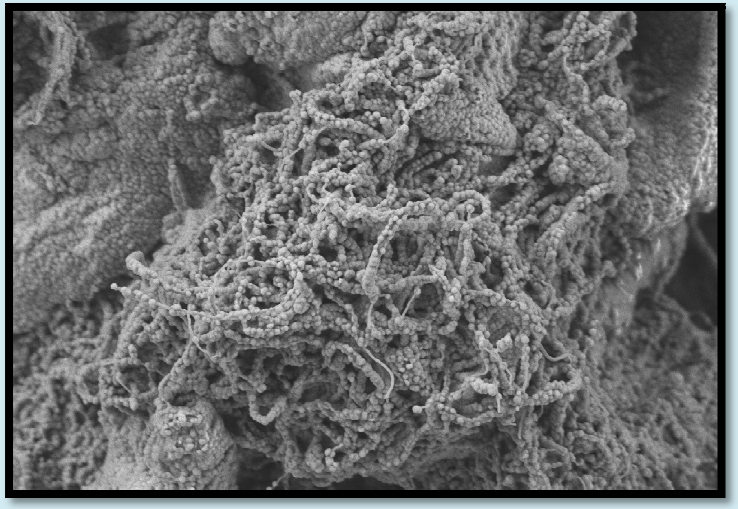
Sample name	Inside coating (5000X)	Inside coating (10000X)
NA23		

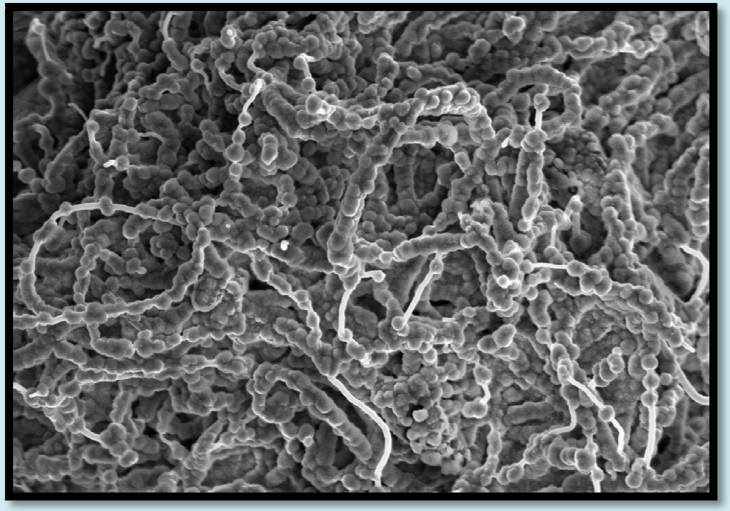
NA33

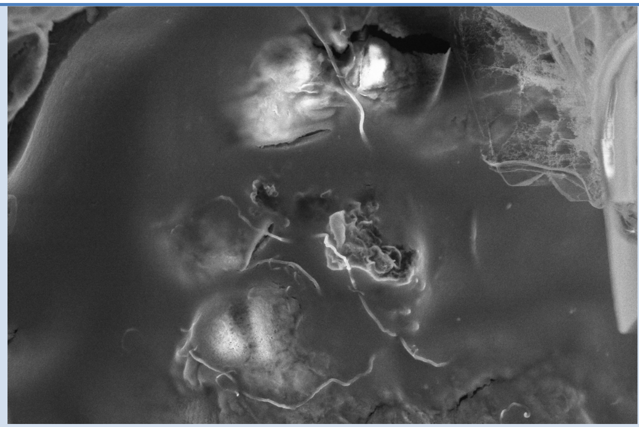
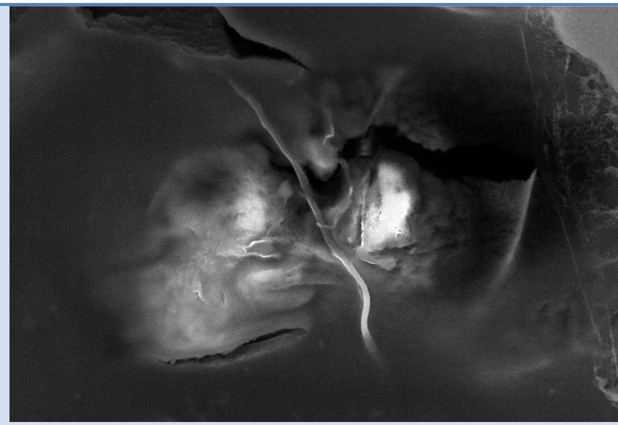
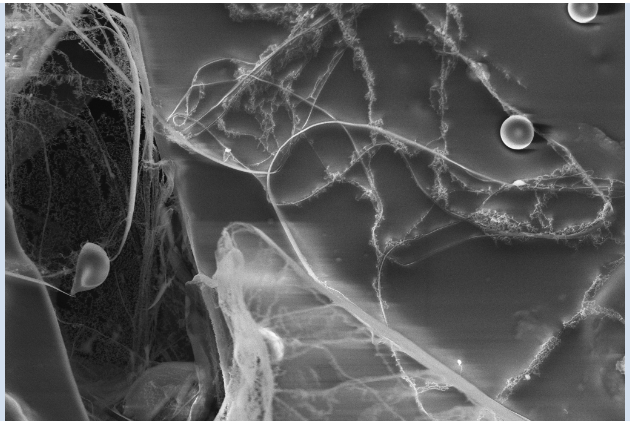
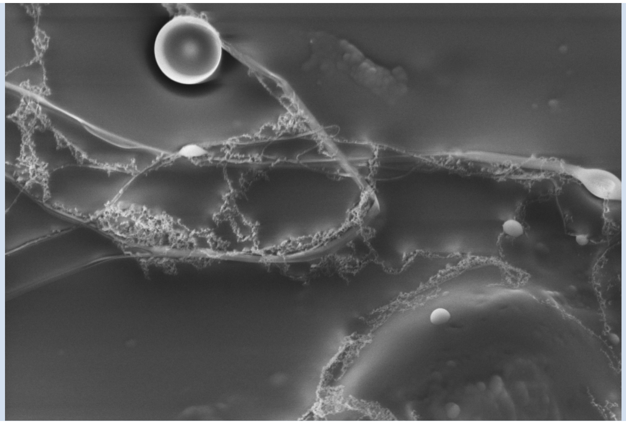




NB27





Sample name	Inside coating (5000X)	Inside coating (10000X)
NB33		
	Outside (5000X)	
		
	At outside coating a bundle of CNT can be seen attach to the char skin. This help in boost in thermal conductivity of the coating	